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Structure and Properties of 9-(Cycloheptatrienylidene)fluorene and Its Derivatives

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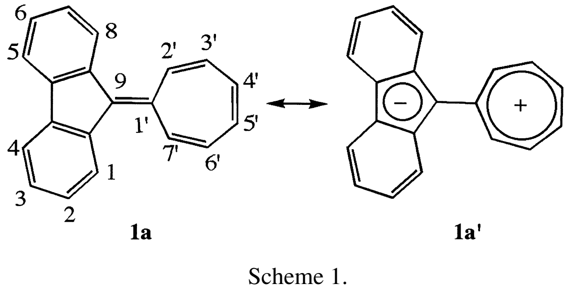
One sesquifulvalene, 9-(cycloheptatrienylidene)fluorene, was found to be composed of a flat fluorenylidene part and a non-planar cycloheptatrienylidene moiety. 1-Substituted 9-(cycloheptatrienylidene)fluorene was not obtained because of a steric repulsion between the 1-substituent and the 7′-hydrogen of the seven-membered ring. Upon consideration of their ^{13}C NMR spectra, the electronic properties of the seven-membered ring are slightly influenced by introducing a substituent (halogen, methoxy group, etc.) on the fluorenylidene part. The dissolution of 9-(cycloheptatrienylidene)fluorene in trifluoroacetic acid–chloroform afforded the (9-fluorenyl)tropylium cation. The substituent attached to the fluorene part also slightly influences the tropylium moiety.

Sesquifulvalene has been actively studied concerning its structure and reactivities since about 1960.[1,2] 9-(Cycloheptatrienylidene)fluorene (**1a**) (Scheme 1) has been reported to be one of the sesquifulvalene derivatives.[2–7] The seven-membered ring of some heptafulvenes has been reported to be planar[8] based on an X-ray analysis and other findings, though there also exist some heptafulvalenes possessing a non-planar seven-membered ring.[1,8–10] The title compound, **1a**, has been treated as a planar molecule[2,4,5] without any clear evidence. When **1a** is a planar sesquifulvalene, the contribution of the dipolar resonance form is important to satisfy the Hückel rule, as in Scheme 1. Compound **1a** and its derivatives are promised precursors of dyes and electronic materials, if there would be a significant participation of a dipolar resonance structure (**1a′**).

The present paper deals with the properties of **1a** and its derivatives that possess substituents at the fluorene moiety, as a part of our continuous studies on the synthesis and characterization of polycyclic aromatic hydrocarbons.[11] The first part of this paper concerns the steric structure of **1a**. Fulvalene **1a** is now found to consist of a flat fluorenylidene part and a non-planar cycloheptatrienylidene moiety. Secondly, we correlate the difficulties in the synthesis of derivatives of **1a** to the non-planarity. The steric repulsion between the 1-substituent of fluorenylidene moiety and the 7′-hydrogen of the seven-membered ring may hamper the formation of the 1-substituted compound, in clear contrast to the syntheses of 9,9′-bifluorenylidene derivatives. The third states the effect of the substituent attached to the fluorenylidene moiety to the seven-membered ring based on their ^{13}C NMR spectra. The electronic properties of the seven-membered ring are slightly affected by the introducing a substituent, such as halogen or methoxy group. The last concerns the substituent effect of the (9-fluorenyl)tropylium cation obtained by a reaction of the dibenzosesquifulvalene **1** with trifluoroacetic acid (TFA). The substituent attached to the fluorene part slightly influences the tropylium moiety.



1a **1a'**

Scheme 1.

Results and Discussion

Based on a molecular model, **1a** is presumed to be non-planar, because of a steric repulsion between the 1-hydrogen of the fluorenylidene part and the 7′-hydrogen of the tropylidene moiety and between the 8-hydrogen and the 2′-hydrogen. In order to release the steric strain, two conformations are possible, as shown in Fig. 1. One is the twisting form[12] at the central double bond between the flat fluorenylidene moiety and the planar seven-membered ring, as in the case of 9,9′-bifluorenylidene.[13] The other is the out-of-plane bending form, in which the flat fluorenylidene part is attached to the folding seven-membered ring.[8,10] The folding structure of the seven-membered ring possesses olefinic properties, or lacks aromatic properties.

We explored a quantum mechanics (PM3) calculation for both candidate structures of **1a**. The heat of formation (ΔH_f) of the bending form was calculated to be 120.1 kcal mol^{-1}, while that of the twisting form was 125.6 kcal mol^{-1}. The former is predicted to be more stable (5.5 kcal) than the latter. The dihedral angle between C(8)–C(1)–C(2)–C(3) (see Fig. 2) is found

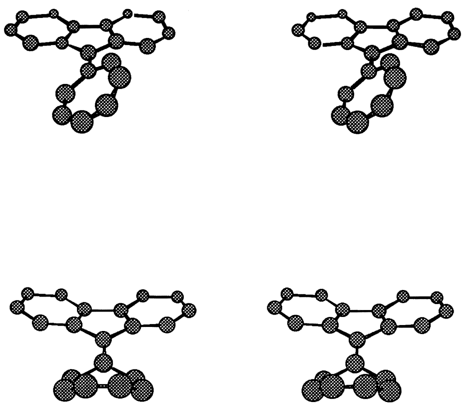


Fig. 1. Symbolic representation (stereoviews) of **1a**. Upper: twisting conformation; lower: bending conformation. Hydrogen atoms are omitted for clarity.

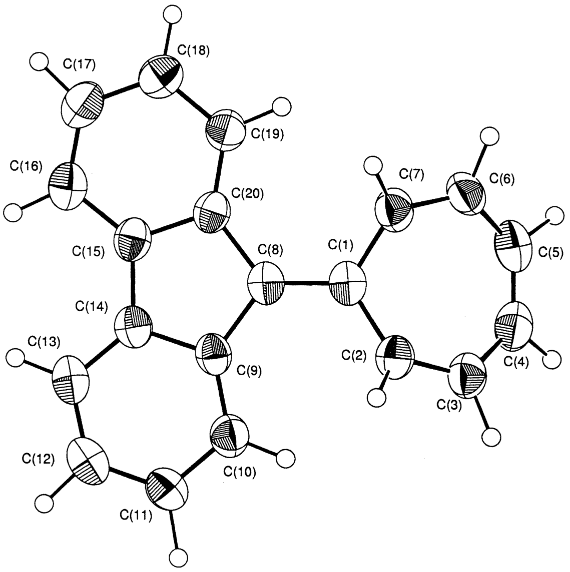
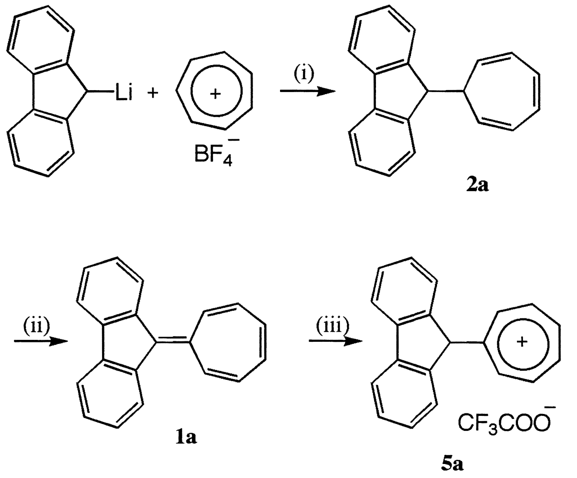


Fig. 2. ORTEP drawing of **1a** with atomic labeling scheme.

Table 1. Crystallographic Data for **1a**

Formula	$C_{20}H_{14}$
Mol wt	254.31
Cryst descript./mm	0.15 × 0.10 × 0.06
Temperature/K	298
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	3.941(2)
b/Å	16.357(11)
c/Å	20.227(11)
β/deg	92.923(3)
V/Å^3	1302.2(13)
Z	4
Calculated density/g cm^{-3}	1.297
Reflections collected	11192
Unique	2532
R_{int}	0.036
F_{000}	536
Limiting indices	$h = 0–4$
	$k = 0–20$
	$1 = -24–+24$
Restraints/parameters	0/237
Goodness of fit (F^2)	1.036
R factor ($I > 2\sigma(I)$)	0.0707
R factor (all data)	0.0932



Scheme 2. Synthesis of **1**: (i) reflux in benzene; (ii) reflux in benzene with DDQ; (iii) TFA.

to be 134.5°. The seven-membered ring showed bond-length alternation. The calculated bond lengths at C(8)–C(1), C(1)–C(2), C(2)–C(3), C(3)–C(4), and C(4)–C(5) were 1.355, 1.458, 1.341, 1.443, and 1.343 Å, respectively. The trend in the bond lengths is quite similar to that obtained by the LCAO-MO-SCF ($\pi + \sigma$) method.[5]

We attempted an X-ray crystallographic analysis of **1a** to elucidate the molecular structure experimentally. Table 1 shows the crystallographic data for **1a**. The selected bond lengths and angles are summarized in Table 2. An ORTEP drawing and the crystal packing projection of **1a** are shown in Figs. 2 and 3, respectively. It is noted that the molecule is made up of a planar fluorenylidene part and a boat-like tropylidene moiety. The dihedral angle between C(8)–C(1)–C(2)–C(3) (see Fig. 2) is found to be about 137°, similar to that of 8,8-dicyano-1,6-dimethylheptafulvene (134.7°) .[8] The bond lengths at C(8)–C(1), C(1)–C(2), C(2)–C(3), C(3)–C(4), and C(4)–C(5) were 1.360, 1.470, 1.342, 1.442, and 1.337 Å, respectively. These values are in good agreement with the calculated ones described above. The bond-length alternation is fairly clearer than that of planar heptafulvene.[8]

Some synthetic procedures of dibenzosesquifulvalene 1 have been reported using three precursors. One is dehydrogenation of 9-(2,4,6-cycloheptatrienyl)fluorene (**2a**).[2] Second is the dehydration of 9-(2,4,6-cycloheptatrienyl)-9-hydroxyfluorene.[14] Third is an elimination of benzenesulfinic acid from 9-(2,4,6-cycloheptatrienyl)-9-fluorenyl benzenesulfinate.[7] The hydrocarbon **2a** is thought to be the most available precursor among them.

The precursor **2a** was easily synthesized by the reaction of 9-lithiofluorene with tropylium tetrafluoroborate[15] in benzene (Scheme 2). According to a similar method, substituted fluorenes afforded derivatives of **2a**, such as 1-methyl-(**2b**), 1-bro-

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1a**[a)]

C(1)–C(2)	1.470(4)	C(1)–C(7)	1.462(4)
C(1)–C(8)	1.360(3)	C(2)–C(3)	1.342(4)
C(3)–C(4)	1.442(4)	C(4)–C(5)	1.337(4)
C(5)–C(6)	1.447(5)	C(6)–C(7)	1.340(4)
C(8)–C(9)	1.486(4)	C(8)–C(20)	1.485(4)
C(9)–C(10)	1.388(4)	C(9)–C(14)	1.411(3)
C(10)–C(11)	1.395(4)	C(11)–C(12)	1.391(4)
C(12)–C(13)	1.386(4)	C(13)–C(14)	1.385(4)
C(14)–C(15)	1.454(3)	C(15)–C(16)	1.395(4)
C(15)–C(20)	1.412(3)	C(16)–C(17)	1.383(4)
C(17)–C(18)	1.391(4)	C(18)–C(19)	1.401(4)
C(19)–C(20)	1.391(4)		
C(2)–C(1)–C(7)	113.8(2)	C(2)–C(1)–C(8)	122.7(3)
C(7)–C(1)–C(8)	123.2(3)	C(1)–C(2)–C(3)	126.6(3)
C(2)–C(3)–C(4)	126.8(4)	C(3)–C(4)–C(5)	126.2(4)
C(4)–C(5)–C(6)	125.7(4)	C(5)–C(6)–C(7)	126.7(4)
C(1)–C(7)–C(6)	126.9(3)	C(1)–C(8)–C(9)	127.2(3)
C(1)–C(8)–C(20)	127.3(3)	C(9)–C(8)–C(20)	105.5(2)
C(8)–C(9)–C(10)	132.6(3)	C(8)–C(9)–C(14)	108.6(3)
C(10)–C(9)–C(14)	118.8(3)	C(9)–C(10)–C(11)	119.7(3)
C(10)–C(11)–C(12)	120.5(3)	C(11)–C(12)–C(13)	120.7(3)
C(12)–C(13)–C(14)	118.6(3)	C(9)–C(14)–C(13)	121.6(3)
C(9)–C(14)–C(15)	108.6(3)	C(13)–C(14)–C(15)	129.8(3)
C(14)–C(15)–C(16)	129.6(3)	C(14)–C(15)–C(20)	109.0(3)
C(16)–C(15)–C(20)	121.4(3)	C(15)–C(16)–C(17)	118.8(4)
C(16)–C(17)–C(18)	120.6(3)	C(17)–C(18)–C(19)	120.8(3)
C(18)–C(19)–C(20)	119.5(3)	C(8)–C(20)–C(15)	108.3(3)
C(8)–C(20)–C(19)	132.7(3)	C(15)–C(20)–C(19)	118.9(3)

a) See Fig. 2 for atomic labeling.

Table 3. Yields and Melting Points of **2** and **1**

Fluorene[a)]	**2**			**1**		
	Compd	Yield/%	Mp/°C	Compd	Yield/%	Mp/°C
	2a	82	110–112	**1a**	81	97–99
1-Methyl	**2b**	68	114–115	—	—	—
1-Bromo	**2c**	63	111.0–112.5	—	—	—
2-Bromo	**2d**	69	113–115	**1d**	87	118.0–118.5
3-Bromo	**2e**	73	51–53	**1e**	81	145–147
4-Bromo	**2f**	60	oil	**1f**	74	104–106
2-Fluoro	**2g**	74	93–95	**1g**	85	118.5–119.0
2-Chloro	**2h**	64	92.5–93.5	**1h**	82	132–133
2-Methyl	**2i**	64	62–64	**1i**	79	105–107
2-Methoxy	**2j**	72	140–142	**1j**	87	140–142
2,7-Dibromo	**2k**	48	164.0–165.5	**1k**	86	176.5–177.0
2,7-Di-*t*-butyl	**2l**	70	105–107	**1l**	87	140–142
2-Bromo-7-*t*-butyl	**2m**	70	99–101	**1m**	86	128–129

a) Positional numbering of substituent is same with Scheme 1.

mo-(**2c**), 2-bromo-(**2d**), 3-bromo-(**2e**), 4-bromo-(**2f**), 2-fluoro-(**2g**), 2-chloro-(**2h**), 2-methyl-(**2i**), 2-methoxy-(**2j**), 2,7-dibromo-(**2k**), 2,7-di-*t*-butyl-(**2l**), and 2-bromo-7-*t*-butyl-9-(2,4,6-cycloheptatrienyl)fluorenes (**2m**). The yields and melting points of these compounds are summarized in Table 3.

While the dehydrogenation of **2a** to **1a** was achieved with trityl fluoroborate/triethylamine, with *N*-bromosuccinimide/triethylamine, or with chloranil,[2] the best result was achieved by a treatment of **2a** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (Scheme 2). Compounds **1d**–**1m** were obtained by reactions of the corresponding precursors, **2d**–**2m**, with DDQ, as are shown in Table 3. In contast, all attempts to form 1-methyl-(**1b**) and 1-bromo derivatives (**1c**) failed, and only oligomers were given. The fact that neither **1b** nor **1c** were obtained is explained by the steric repulsion between the 1-substituent of fluorenylidene moiety and the 7′-hydrogen of

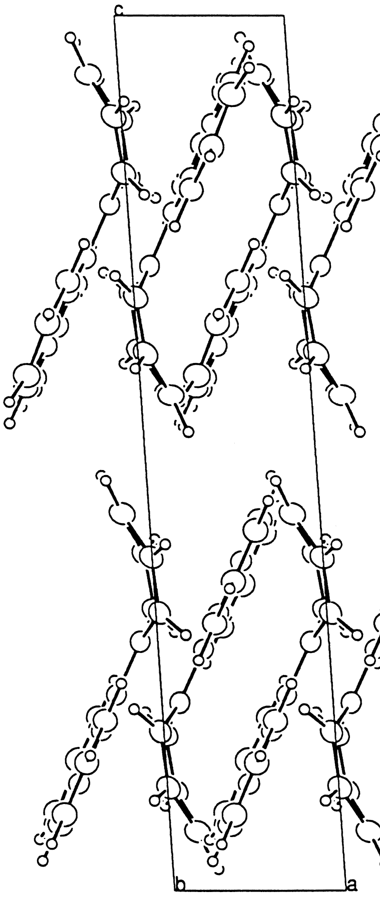


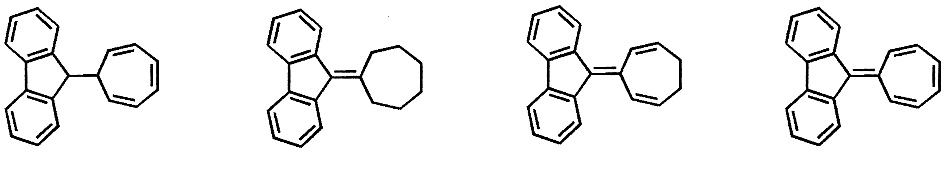
Fig. 3. Crystal packing projection for **1a** viewed along *b* axis.

the seven-membered ring, as in the case of the dehydrobromination of 9-bromo-9-(2,4,6,8-cyclononatetraenyl)fluorene.[16] This interpretation is consistent with the NMR spectra (next paragraph) and the calculated data. The dehydrogenation of fulvalenes **1b** and **1c** was less favorable than the parent **1a**. The enthalpy changes in going from **2b** to **1b** and from **2c** to **1c** (20.4 and 19.0 kcal mol^{-1}, respectively endothermic) were larger than those in going from **2a** to **1a** and from **2d**–**2m** to **1d**–**1m** (16.3–16.6 kcal mol^{-1}, endothermic).

The NMR data of **2** also support **1b** and **1c** to be sterically less stable than the others. In the ^{1}H NMR spectra of **2d**–**2m**, four groups of signals are assigned to the H(1′), H(2′, 7′), H(3′, 6′), and H(4′, 5′) of the seven-membered ring, just the same as **2a**.[2] The ^{13}C NMR spectrum of **2a** also gave four signals, which arose from the seven-membered ring (C(1′), C(2′, 7′), C(3′, 6′), and C(4′, 5′)). The symmetrical **2k** and **2l** also show four ^{13}C NMR signals corresponding to the seven-membered ring carbons. Although compounds **2d**–**2j**, and **2m**, possessing an asymmetrical fluorene part, show apparently six or seven signals, the differences ($\Delta\delta$) of chemical shifts between the signals of seven-membered ring, for example $\Delta\delta$ between the C(2′) and the C(7′), are within only 0.1 ppm. This suggests that **2a** and **2d**–**2m** possess essentially a common structure of the seven-membered ring, which is slightly affected by the substituents on the fluorene moiety. On the contrary, seven sets of ^{1}H NMR signals have been separately recorded for the seven-membered ring protons in the cases of **2b** and **2c**. The ^{13}C NMR peak of the C(1′) of **2b** and **2c** locates more upperfield (ca. 3 ppm) than that of **2a**. The $\Delta\delta$ between the C(2′) and the C(7′) of **2b** and **2c** are larger than 3 ppm. This strongly suggests that the seven-membered rings of **2b** and **2c** suffer from distortion by the substituent attached to the C(1) on the fluorene moiety.

In solution, the bending form (lower in Fig. 1) of **1a** is assumed to be in equilibrium with the twisting form (upper in Fig. 1), and the equilibrium may lie to the former conformation. The UV absorption maxia of **1a** has been reported to be dependent on the kind of solvent used.[2] The longest absorption maximum in the electronic spectrum of **1a** is compared with those of **2a**, 9-(cycloheptylidene)fluorene (**3a**), and 9-(2,6-cycloheptadienylidene)fluorene (**4a**), as shown in Scheme 3. The conversion of **2a** to **1a** results in a red shift (72 nm). The difference (31 nm) of the absorption maximum between **1a** and **4a** is slightly larger than that (23 nm) between **4a** and **3a**. The longest absorption maximum of **1a** is situated at a shorter wavelength than those of 1-(cycloheptatrienylidene)indene and 3-benzyl-1-(cycloheptatrienylidene)cycloheptadiene.[3] This suggests a limited aromaticity contributed from the twisting form existing as a minor conformation in equilibrium with the bending form.

Signals on the ^{1}H NMR[2] and ^{13}C NMR[6] of **1a** in CDCl$_3$ are assigned by combination of COSY and hetero COSY techniques and a comparison with the spectra obtained in C$_6$D$_6$ as a solvent. The ^{1}H NMR spectrum of the seven-membered ring of **1a** shows two complex patterns due to the H(2′, 7′) and H(3′, 4′, 5′, 6′). The chemical shifts of the C(9), C(1′), C(2′, 7′), C(3′, 6′), and C(4′, 5′) are observed at δ 129.4, 136.0, 129.8, 129.0, and 132.5 ppm, respectively. The assignment of the seven-membered ring carbons differs from that in the liter-



	2a	**3a**	**4a**	**1a**
λ (nm)	303	321	344	375
log ε	3.8	4.3	4.6	3.7

Scheme 3. The longest absorption maxima of **1a** and related compounds.

ature.[6]

The substituent attached to the fluorene moiety also gives an electronic influence to the seven-membered ring. The chemical shifts of the seven-membered ring protons of **1d–1m** are apparently similar to those of **1a**. The differences (Δδ) of each chemical shift of the seven-membered ring carbons of **1d–1m** compared to the corresponding carbon of **1a** are within −2.5 to +1.1 ppm for the C(9), −1.5 to +2.5 ppm for the C(1′), −0.7 to +0.5 ppm for the C(2′, 7′), −0.5 to +0.8 ppm for the C(3′, 6′), and 0 to +0.5 ppm for the C(4′, 5′). The Δδ between the C(1′) and C(9) is 6.6 ppm for **1a**, while the values are 11.6 and 4.0 ppm for **1k** and **1l**, respectively. This tendency can be interpreted as meaning that the introduction of electron-withdrawing bromine in the fluorenylidene part slightly increases the polarity between the C(9)–C(1′) bond, while the *t*-butyl group decreases the polarity. This view is further supported by the fact that the Hammett constants of these substituents are proportional to the difference between the calculated electronic charges at C(9) and C(1′) (data not shown).

The dissolution of **1a** in TFA at room temperature gave (9-fluorenyl)tropylium trifluoroacetate (**5a**).[2,7] Dilution of the solution with water yielded **1a** quantitatively. The chemical shifts of the seven-membered ring carbons of **5a** appear at δ 178.2 ppm for C(1′), 155.3 ppm for C(2′, 7′), and 153.8/153.5 ppm for C(3′–6′) using TFA–CDCl$_3$ (1/1) as solvent. The shifts at the C(2′–7′) are similar to that of the parent tropylium cation (δ 155.4 ppm).[17] The Δδ between the C(4′ or 3′) and C(2′) of **5a** is 1.8 ppm and that between the C(4′) and C(3′) is 0.3 ppm. On the other hand, the values between C(4′ or 3′) and C(2′) and between C(4′) and C(3′) of **1a** are 2.7 and 3.5 ppm, respectively. The small Δδ of **5a** indicates that the seven-membered ring of **5a** is more planar and the charge is more delocarized over the ring of **5a**, than those of **1a**.

The chemical shifts of the seven-membered ring carbons of **5d–5m** derived from **1d–1m**, respectively, differ by −2.4 to +1.4 ppm at the C(1′) and −0.1 to +0.6 ppm at C(2′–7′), respectively, from those of **5a**. The Δδ between the C(4′ or 3′) and C(2′) of **5k** is 1.2 ppm and that between the C(4′) and C(3′) is 0.1 ppm, which is smaller than the values of **5l** (1.9 and 0.2 ppm between the C(4′) and C(2′) and between the C(4′) and C(3′), respectively). The difference between **5k** and **5l** suggests that a delocalization of the charge is more facile in **5k** than in **5a**. The substituent attached to the fluorene part slightly influences the tropylium moiety.

Experimental

The melting points (Table 1) are uncorrected. The NMR (CDCl$_3$) and UV-visible (EtOH) spectra were recorded with a Varian VXR-300 and a JASCO V-560. Only the assigned chemical shifts were designated in parentheses. The mass spectra and elemental analyses were measured with a JMX-AX 500 (JEOL) and with an EA 1108 CHNS-O (Fison Instruments), respectively.

The conformations of the molecules were estimated using a molecular-mechanics program in Chem 3D pro (CambridgeSoft Corp.) on a Macintosh Performa 6260. The optimized molecular structures were also examined using molecular-mechanics program MM+ and the quantum-mechanics program PM3 packed in Hyper Chem release 5.1 (Hyper Cube Inc.). The parameters were employed without any modification, and the calculations were performed on a computer (Dell Dimension XPS T-500). Geometry optimization by Hyper Chem employed the Polak–Ribiera method, and the calculation ran until the root–mean–square gradient reached a value less than 0.01 kcal/Å mol.

X-ray Crystallographic Analysis. A single crystal was grown in a hexane solution. The intensity data were collected at 298 K on a MAC Science DIPlabo imaging-plate area detector with graphite-monochromaized Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The structure was solved by the direct method (SIR97) and refined by full-matrix least-squares techniques. All hydrogen atoms were located by difference Fourier syntheses and include in the refinement with isotropic thermal parameters. The final *R* factor was 0.0707 ($_wR = 0.1825$) for 1788 reflections with $I_o > 2\sigma(I_o)$. All diagrams and calculations were performed using maXus.[18] The crystal data and experimental details are listed in Table 1.

9-(2,4,6-Cycloheptatrienyl)fluorene (2a). Typical procedure. To a mixture of fluorene (4.98 g, 30 mmol) in ether (100 mL) was dropped BuLi (1.6 M hexane, 19.4 mL, 31 mmol) at −5 °C under an atmosphere of argon; the whole was stirred at 0 °C for 2 h. Tropylium tetrafluoroborate (5.33 g, 30 mmol) suspended in benzene (100 mL) was added to the resulting mixture. Upon the evaporation of ether, the mixture was refluxed for 8 h. After the usual treatment, the crude product was chromatographed on silica gel with benzene to give **2a** (6.31 g, 82%): Mp 110–112 °C (from ethanol) (Ref. 2, mp 108–109 °C); ^{1}H NMR δ 2.52–2.54 (H$_{1'}$), 4.31 (d, *J* = 4.8 Hz, H$_9$), 5.21–5.26 (H$_{2'}$, H$_{7'}$), 6.16–6.21 (H$_{3'}$, H$_{6'}$), 6.63–6.65 (H$_{4'}$, H$_{5'}$), 7.28 (t, *J* = 8.4 Hz, H$_2$, H$_7$), 7.39 (t, *J* = 8.4 Hz, H$_3$, H$_6$), 7.57 (d, *J* = 8.4 Hz, H$_4$, H$_5$), 7.79 (d, *J* = 7.5 Hz, H$_1$, H$_8$); ^{13}C NMR δ 42.5 (C$_{1'}$), 48.2 (C$_9$), 119.6 (C$_1$, C$_8$), 125.0 (C$_4$, C$_5$), 125.0 (C$_{2'}$, C$_{7'}$), 125.5 (C$_{3'}$, C$_{6'}$), 126.8 (C$_2$, C$_7$), 127.2 (C$_3$, C$_6$), 130.8 (C$_{4'}$, C$_{5'}$), 141.6 (C$_{8a}$, C$_{9a}$), 145.8 (C$_{4a}$, C$_{4b}$).

2b. ^{1}H NMR δ 2.32 (Me), 2.71–2.76 (H$_{1'}$), 4.16 (dd, *J* = 9.5, 5.3 Hz, H$_{2'}$), 4.48 (d, *J* = 2.7 Hz, H$_9$), 5.82 (dd, *J* = 9.5, 5.4 Hz, H$_{3'}$), 5.95 (dd, *J* = 9.5, 5.6 Hz, H$_{7'}$), 6.31 (dd, *J* = 9.5, 5.3 Hz, H$_{6'}$), 6.52 (dd, *J* = 10.5, 5.4 Hz, H$_{4'}$), 6.61 (dd, *J* = 10.5, 5.3 Hz, H$_{5'}$), 7.06 (d, *J* = 7.5 Hz, H$_2$), 7.26 (t, *J* = 7.2 Hz, H$_6$), 7.29 (t, *J* = 7.7 Hz, H$_3$), 7.39 (t, *J* = 7.4 Hz, H$_7$), 7.63 (d, *J* = 7.8 Hz, H$_4$), 7.66 (d, *J* = 7.7 Hz, H$_8$), 7.78 (d, *J* = 7.5 Hz, H$_5$); ^{13}C NMR δ 19.1 (Me), 39.8 (C$_{1'}$), 48.9 (C$_9$), 117.2 (C$_4$), 119.8 (C$_5$), 123.6 (C$_{2'}$), 124.9 (C$_{3'}$), 125.3 (C$_{6'}$), 125.5 (C$_8$), 126.4 (C$_{7'}$), 127.3 (C$_7$), 127.4 (C$_3$), 129.1 (C$_2$), 129.9 (C$_{5'}$), 131.1 (C$_{4'}$), 134.2 (C$_1$), 141.4 (C$_{4a}$), 142.4 (C$_{8a}$), 144.1 (C$_{9a}$), 145.2 (C$_{4b}$); MS *m/z* 270 (M$^+$), 179, 91. Found: C, 93.43; H, 6.78%. Calcd for C$_{21}$H$_{18}$: C, 93.29; H, 6.71%.

2c. ^{1}H NMR δ 3.21–3.26 (H$_{1'}$), 4.10 (dd, *J* = 9.3, 5.3 Hz, H$_{2'}$), 4.52 (d, *J* = 3.1 Hz, H$_9$), 5.82 (dd, *J* = 9.3, 5.3 Hz, H$_{3'}$), 5.93 (dd, *J* = 9.3, 5.3 Hz, H$_{7'}$), 6.33 (dd, *J* = 9.3, 5.3 Hz, H$_{6'}$), 6.53 (dd, *J* = 11.1, 5.3 Hz, H$_{4'}$), 6.62 (dd, *J* = 11.1, 5.3 Hz, H$_{5'}$), 7.25 (d, *J* = 7.5 Hz, H$_3$), 7.32 (t, *J* = 7.5 Hz, H$_7$), 7.40 (d, *J* = 7.5 Hz, H$_2$), 7.42 (t, *J* = 7.5 Hz, H$_6$), 7.68 (d, *J* = 7.5 Hz, H$_8$), 7.72 (d, *J* = 7.5 Hz, H$_4$), 7.78 (d, *J* = 7.5 Hz, H$_5$); ^{13}C NMR δ 38.9 (C$_{1'}$), 50.8 (C$_9$), 118.5 (C$_4$), 119.9 (C$_1$), 120.2 (C$_5$), 123.0 (C$_{2'}$), 125.1 (C$_{3'}$), 125.5 (C$_{6'}$), 125.6 (C$_8$), 126.0 (C$_{7'}$), 127.6 (C$_7$), 127.6 (C$_6$), 129.1 (C$_3$), 130.1 (C$_{5'}$), 131.0 (C$_2$), 131.1 (C$_{4'}$), 141.3 (C$_{4b}$), 143.7 (C$_{4a}$), 144.6 (C$_{9a}$), 144.9 (C$_{8a}$); MS *m/z* 336, 334 (M$^+$), 245, 243, 164, 91. Found: C, 71.78; H, 4.59%. Calcd for C$_{20}$H$_{15}$Br: C, 71.65; H, 4.51%.

2d. ^{1}H NMR δ 2.50–2.52 (H$_{1'}$), 4.27 (d, *J* = 4.8 Hz, H$_9$), 5.17–5.26 (H$_{2'}$, H$_{7'}$), 6.20–6.24 (H$_{3'}$, H$_{6'}$), 6.66–6.68 (H$_{4'}$, H$_{5'}$), 7.30 (t, *J* = 7.5 Hz, H$_7$), 7.40 (t, *J* = 7.5 Hz, H$_6$), 7.51 (d, *J* = 8.1 Hz, H$_3$), 7.56 (d, *J* = 7.5 Hz, H$_8$), 7.64 (d, *J* = 8.1 Hz, H$_4$), 7.69 (d, *J* = 1.8 Hz, H$_1$), 7.76 (d, *J* = 7.5 Hz, H$_5$); ^{13}C NMR δ 42.3

($C_{1'}$), 48.0 (C_9), 119.7 (C_5), 120.6 (C_2), 120.9 (C_4), 124.4 ($C_{2'}$ or $C_{7'}$), 124.5 ($C_{2'}$ or $C_{7'}$), 125.1 (C_8), 125.8, 127.2 (C_7), 127.4 (C_6), 128.3 (C_1), 130.3 (C_3), 130.8, 130.9, 140.5 (C_{4a}), 140.5 (C_{4b}), 145.5 (C_{8a}), 147.9 (C_{9a}); MS *m/z* 336, 334 (M^+), 245, 243, 91. Found: C, 71.41; H, 4.48%. Calcd for $C_{20}H_{15}Br$: C, 71.65; H, 4.51%.

2e. ^{1}H NMR δ 2.46–2.52 ($H_{1'}$), 4.24 (d, J = 4.8 Hz, H_9), 5.16–5.25 ($H_{2'}$, $H_{7'}$), 6.18–6.23 ($H_{3'}$, $H_{6'}$), 6.65 (t, J = 2.9 Hz, $H_{4'}$, $H_{5'}$), 7.31 (t, J = 7.5 Hz, H_7), 7.37–7.42 (H_2, H_6), 7.42–7.45 (H_1), 7.58 (d, J = 7.5 Hz, H_8), 7.75 (d, J = 7.5 Hz, H_5), 7.90 (d, J = 1.5 Hz, H_4); ^{13}C NMR δ 42.4 ($C_{1'}$), 47.8 (C_9), 119.9 (C_5), 121.4 (C_3), 122.9 (C_4), 124.5 ($C_{2'}$ or $C_{7'}$), 124.6 ($C_{2'}$ or $C_{7'}$), 125.2 (C_8), 125.7, 126.5 (C_1), 127.5 (C_6), 127.6(C_7), 129.6 (C_2), 130.8, 130.9, 140.3 (C_{4b}), 143.7 (C_{9a}), 144.6 (C_{4a}), 146.1 (C_{8a}); MS *m/z* 336, 334 (M^+), 245, 243, 164, 163, 91.

2f. ^{1}H NMR δ 2.52–2.55 ($H_{1'}$), 4.31 (J = 4.5 Hz, H_9), 5.12–5.28 ($H_{2'}$, $H_{7'}$), 6.17–6.21 ($H_{3'}$, $H_{6'}$), 6.63–6.66 ($H_{4'}$, $H_{5'}$), 7.12 (t, J = 7.8 Hz, H_2), 7.35 (t, J = 7.5 Hz, H_7), 7.45 (t, J = 7.5 Hz, H_6), 7.49–7.57 (H_1, H_3), 7.59 (d, J = 7.5 Hz, H_8), 8.67 (d, J = 7.5 Hz, H_5); ^{13}C NMR δ 42.8 ($C_{1'}$), 48.2 (C_9), 116.8 (C_4), 123.3 (C_5), 123.8 (C_3), 124.7 ($C_{2'}$ or $C_{7'}$), 124.8 ($C_{2'}$ or $C_{7'}$), 124.8 (C_8), 125.7, 127.0 (C_6), 127.5 (C_7), 127.6 (C_2), 130.8, 130.8, 132.4 (C_1), 139.6 (C_{4a}), 140.9 (C_{4b}), 146.2 (C_{8a}), 148.9 (C_{9a}); MS *m/z* 336, 334 (M^+), 245, 243, 164, 163, 91. Found: C, 71.43; H, 4.77%. Calcd for $C_{20}H_{15}Br$: C, 71.65; H, 4.51%.

2g. ^{1}H NMR δ 2.49–2.52 ($H_{1'}$), 4.26 (d, J = 4.8 Hz, H_9), 5.17–5.29 ($H_{2'}$, $H_{7'}$), 6.20–6.25 ($H_{3'}$, $H_{6'}$), 6.65–6.67 ($H_{4'}$, $H_{5'}$), 7.08 (ddd, J = 8.7, 8.4, 2.4 Hz, H_3), 7.24–7.29 (H_1, H_6), 7.39 (t, J = 7.5 Hz, H_7), 7.56 (d, J = 7.5 Hz, H_8), 7.71 (dd, J = 8.4, 5.1 Hz, H_4), 7.73 (d, J = 7.5 Hz, H_5); ^{13}C NMR δ 42.4 ($C_{1'}$), 48.0 (d, J = 2.0 Hz, C_9), 112.5 (d, J = 23.0 Hz, C_1), 114.4 (d, J = 22.9 Hz, C_3), 119.3 (C_5), 120.5 (d, J = 8.8 Hz, C_4), 124.5 ($C_{2'}$ or $C_{7'}$), 124.6 ($C_{2'}$ or $C_{7'}$), 125.1 (C_8), 125.8, 125.8, 126.5 (C_6), 127.4 (C_7), 130.8, 130.9, 137.5 (d, J = 2.3 Hz, C_{4a}), 140.7 (C_{4b}), 145.7 (d, J = 1.9 Hz, C_{8a}), 148.0 (d, J = 8.1 Hz, C_{9a}), 162.2 (d, J = 243 Hz, C_2); MS *m/z* 274 (M^+), 183, 91. Found: C, 87.37; H, 5.63%. Calcd for $C_{20}H_{15}F$: C, 87.56; H, 5.51%.

2h. ^{1}H NMR δ 2.50–2.52 ($H_{1'}$), 4.27 (d, J = 4.8 Hz, H_9), 5.17–5.27 ($H_{2'}$, $H_{7'}$), 6.20–6.24 ($H_{3'}$, $H_{6'}$), 6.66–6.68 ($H_{4'}$, $H_{5'}$), 7.29 (t, J =7.5 Hz, H_7), 7.36(d, J = 8.1 Hz, H_3), 7.40 (t, J = 7.5 Hz, H_6), 7.54 (d, J = 1.8 Hz, H_1), 7.56 (d, J = 7.5 Hz, H_5), 7.69 (d, J = 8.1 Hz, H_4), 7.75 (d, J = 7.5 Hz, H_8); ^{13}C NMR δ 42.4 ($C_{1'}$), 48.0 (C_9), 119.7 (C_8), 120.5 (C_4), 124.5 ($C_{2'}$ or $C_{7'}$), 124.5 ($C_{2'}$ or $C_{7'}$), 125.2 (C_5), 125.5 (C_1), 125.8, 125.8, 127.1 (C_7), 127.4 (C_6), 127.5 (C_3), 130.8, 130.9, 132.5 (C_2), 140.1 (C_{4a}), 140.5 (C_{4b}), 145.7 (C_{8a}), 147.6 (C_{9a}); MS *m/z* 292, 290 (M^+), 201, 199, 91. Found: C, 82.75; H, 5.21%. Calcd for $C_{20}H_{15}Cl$: C, 82.61; H, 5.20%.

2i. ^{1}H NMR δ 2.41 (Me), 2.51–2.57 ($H_{1'}$), 4.28 (d, J = 4.5 Hz, H_9), 5.18–5.26 ($H_{2'}$, $H_{7'}$), 6.16–6.20 ($H_{3'}$, $H_{6'}$), 6.64 (t, J = 2.9 Hz, $H_{4'}$, $H_{5'}$), 7.20 (t, J = 7.8 Hz, H_3), 7.25(t, J = 7.6 Hz, H_7), 7.37 (t, J = 7.6 Hz, H_6), 7.37 (d, J = 0.9 Hz, H_1), 7.53 (d, J = 7.6 Hz, H_8), 7.67 (d, J = 7.8 Hz, H_4), 7.74 (d, J = 7.6 Hz, H_5); ^{13}C NMR δ 21.9 (Me), 42.5 ($C_{1'}$), 48.2 (C_9), 119.3 (C_5), 119.4 (C_4), 124.9 (C_8), 125.1 ($C_{2'}$ or $C_{7'}$), 125.5, 125.7 (C_1), 126.4 (C_7), 127.2 (C_6), 128.1 (C_3), 130.7, 136.7 (C_2), 139.0 (C_{4a}), 141.7 (C_{4b}), 145.6 (C_{8a}), 146.0 (C_{9a}); MS *m/z* 270 (M^+), 179, 91. Found: C, 93.40; H, 6.61%. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.71%.

2j. ^{1}H NMR δ 2.49–2.53 ($H_{1'}$), 3.84 (Me), 4.26 (d, J = 4.5 Hz, H_9), 5.15–5.31 ($H_{2'}$, $H_{7'}$), 6.15–6.22 ($H_{3'}$, $H_{6'}$), 6.64 (t, J = 3.3 Hz, $H_{4'}$, $H_{5'}$), 6.94 (dd, J = 8.1, 2.4 Hz, H_3), 7.10 (d, J = 2.4 Hz, H_1), 7.21 (d, J = 7.5 Hz, H_7), 7.35 (t, J = 7.5 Hz, H_6), 7.53 (d, J = 7.5 Hz, H_8), 7.68 (d, J = 8.1 Hz, H_4), 7.69 (d, J = 7.5 Hz, H_5); ^{13}C NMR δ 42.6 ($C_{1'}$), 48.2 (C_9), 55.4 (Me), 111.1 (C_1), 112.9 (C_3), 118.9 (C_5), 120.3 (C_4), 124.8 ($C_{2'}$ or $C_{7'}$), 125.0 ($C_{2'}$ or $C_{7'}$), 125.0 (C_8), 125.5, 125.6, 125.7 (C_7), 127.2 (C_6), 130.7, 130.8, 134.6 (C_{4a}), 141.6 (C_{4b}), 145.3 (C_{8a}), 147.7 (C_{9a}), 159.2 (C_2); MS *m/z* 286 (M^+), 195, 91. Found: C, 88.02; H, 6.30%. Calcd for $C_{21}H_{18}O$: C, 88.08; H, 6.34%.

2k. ^{1}H NMR δ 2.49–2.51 ($H_{1'}$), 4.21 (d, J = 5.4 Hz, H_9), 5.19–5.24 ($H_{2'}$, $H_{7'}$), 6.25–6.30 ($H_{3'}$, $H_{6'}$), 6.68–6.71 ($H_{4'}$, $H_{5'}$), 7.52 (d, J = 1.8 Hz, H_1, H_8), 7.61 (d, J = 8.1 Hz, H_4, H_5), 7.69 (d, J = 8.1 Hz, H_3, H_6); ^{13}C NMR δ 42.2 ($C_{1'}$), 47.6 (C_9), 121.0 (C_4, C_5), 121.1 (C_2, C_7), 124.0 ($C_{2'}$, $C_{7'}$), 126.1 ($C_{3'}$, $C_{6'}$), 128.5 (C_3, C_6), 130.6 (C_1, C_8), 131.0 ($C_{4'}$, $C_{5'}$), 139.5 (C_{4a}, C_{4b}), 147.7 (C_{8a}, C_{9a}); MS *m/z* 416, 414, 412 (M^+), 325, 323, 321, 91. Found: C, 58.13; H, 3.50%. Calcd for $C_{20}H_{14}Br_2$: C, 58.00; H, 3.41%.

2l. ^{1}H NMR δ 1.35 (Bu), 2.45–2.52 ($H_{1'}$), 4.23 (d, J = 4.8 Hz, H_9), 5.26–5.31 ($H_{2'}$, $H_{7'}$), 6.19–6.24 ($H_{3'}$, $H_{6'}$), 6.67 (t, J = 2.7 Hz, $H_{4'}$, $H_{5'}$), 7.40 (dd, J = 7.8, 2.7 Hz, H_3, H_6), 7.56 (d, J = 2.7 Hz, H_1, H_8), 7.66 (d, J = 7.8 Hz, H_4, H_5); ^{13}C NMR δ 31.5 (Me), 34.7, 42.8 ($C_{1'}$), 48.1 (C_9), 118.8 (C_4, C_5), 121.9(C_1, C_8), 124.2 (C_3, C_6), 125.3 ($C_{3'}$, $C_{6'}$), 125.3 ($C_{2'}$, $C_{7'}$), 130.7 ($C_{4'}$, $C_{5'}$), 138.9 (C_{4a}, C_{4b}), 145.9 (C_{8a}, C_{9a}), 149.5 (C_2, C_7); MS *m/z* 368 (M^+), 277, 91. Found: C, 91.05; H, 8.73%. Calcd for $C_{28}H_{32}$: C, 91.25; H, 8.75%.

2m. ^{1}H NMR δ 1.35 (Bu), 2.46–2.52 ($H_{1'}$), 4.22 (d, J = 4.8 Hz, H_9), 5.20–5.29 ($H_{2'}$, $H_{7'}$), 6.21–6.27 ($H_{3'}$, $H_{6'}$), 6.68 (t, J = 3.3 Hz, $H_{4'}$, $H_{5'}$), 7.43 (d, J = 8.1 Hz, H_6), 7.48 (d, J = 8.1 Hz, H_3), 7.56 (t, J = 0.6 Hz, H_8) 7.60 (d, J = 8.1 Hz, H_4), 7.67 (t, J = 0.6 Hz, H_1), 7.67 (d, J = 8.1 Hz, H_5); ^{13}C NMR δ 31.4 (Me), 34.8, 42.5 ($C_{1'}$), 47.9 (C_9), 119.2 (C_5), 120.1 (C_2), 120.6 (C_4), 122.1 (C_8), 124.6 (C_6), 124.6 ($C_{2'}$ or $C_{7'}$), 124.6 ($C_{2'}$ or $C_{7'}$), 125.6, 125.7, 128.3 (C_1), 130.3 (C_3), 130.8, 130.9, 137.9 (C_{4b}), 140.5 (C_{4a}), 145.5 (C_{8a}), 148.1 (C_{9a}), 150.6 (C_7); MS *m/z* 392, 390 (M^+), 301, 299, 91. Found: C, 73.93; H, 5.87%. Calcd for $C_{24}H_{23}Br$: C, 73.66; H, 5.92%.

9-(2,4,6-Cycloheptatrienylidene)fluorene (1a). Typical procedure. A solution of **2a** (1.28 g, 5 mmol) and DDQ (1.25 g, 5.5 mmol) in dry benzene (100 mL) was refluxed for 4 h under an atmosphere of argon. Upon filtration, the filtrate was chromatographed on alumina with benzene to give 1.03 g (81%) of **1a**: Mp 97–99 °C (from ethanol) (Ref. 2, mp 96.5 °C); ^{1}H NMR δ 6.49–6.55 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.94–6.98 ($H_{2'}$, $H_{7'}$), 7.25 (dd, J = 7.5, 0.9 Hz, H_2, H_7), 7.31 (dd, J = 7.5, 0.9 Hz, H_3, H_6), 7.75 (dd, J = 7.5, 0.9 Hz, H_4, H_5), 7.95 (dd, J = 7.5, 0.9 Hz, H_1, H_8); ^{13}C NMR δ 119.5 (C_4, C_5), 124.6 (C_1, C_8), 126.4 (C_2, C_7), 126.7 (C_3, C_6), 129.0 ($C_{3'}$, $C_{6'}$), 129.4 (C_9), 129.8 ($C_{2'}$, $C_{7'}$), 132.5 ($C_{4'}$, $C_{5'}$), 136.0 ($C_{1'}$), 138.4 (C_{8a}, C_{9a}), 139.6 (C_{4a}, C_{4b}).

1d. ^{1}H NMR δ 6.50–6.60 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.89–6.99 ($H_{2'}$, $H_{7'}$), 7.29–7.31 (H_7), 7.31–7.33 (H_6), 7.44 (dd, J = 8.1, 1.8 Hz, H_3), 7.61 (d, J = 8.1 Hz, H_4), 7.72 (dd, J = 6.6, 2.1 Hz, H_5), 7.95 (dd, J = 6.6, 2.1 Hz, H_8), 8.08 (d, J = 1.8Hz, H_1); ^{13}C NMR δ 119.6 (C_5), 120.2 (C_2), 120.7 (C_4), 124.5 (C_8), 126.8 (C_7), 126.8 (C_6), 127.3 (C_1), 128.2 (C_9), 129.2 ($C_{2'}$ or $C_{7'}$), 129.3 (C_3), 129.4, 129.6 ($C_{2'}$ or $C_{7'}$), 129.8, 132.7 ($C_{4'}$, $C_{5'}$), 137.3 ($C_{1'}$), 138.1 (C_{8a}), 138.3 (C_{4a}), 138.5 (C_{4b}), 140.0 (C_{9a}); MS *m/z* 334, 332 (M^+).

1e. ^{1}H NMR δ 6.49–6.56 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.87–6.97 ($H_{2'}$, $H_{7'}$), 7.27–7.33 (H_7), 7.30–7.34 (H_6), 7.37 (dd, J = 8.4, 1.8 Hz, H_2), 7.70–7.73 (H_5), 7.81 (d, J = 8.4 Hz, H_1), 7.86 (d, J = 1.8 Hz, H_4), 7.94–7.97 (H_8); ^{13}C NMR δ 119.8 (C_5), 120.8 (C_3), 122.7 (C_4), 124.6 (C_8), 125.6 (C_1), 126.8 (C_6), 127.1 (C_7), 127.6 (C_9), 129.0 (C_2), 129.4, 129.5, 129.6 ($C_{2'}$ or $C_{7'}$), 129.8 ($C_{2'}$ or $C_{7'}$), 132.7, 132.8, 136.8 ($C_{1'}$), 137.0 (C_{9a}), 138.3 (C_{4b}), 138.6 (C_{8a}), 141.4 (C_{4a}); MS *m/z* 334, 332 (M^+), 253. Found: C, 72.37; H, 4.19%. Calcd for $C_{20}H_{13}Br$: C, 72.09; H, 3.93%.

1f. ^{1}H NMR δ 6.49–6.59 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.88–6.95 ($H_{2'}$, $H_{7'}$), 7.10 (d, *J* = 7.8 Hz, H_2), 7.31–7.35 (H_7), 7.36–7.41 (H_6), 7.48 (dd, *J* = 7.8, 0.8 Hz, H_1), 7.96 (d, *J* = 7.8 Hz, H_3), 8.00 (d, *J* = 7.2 Hz, H_8), 8.71 (d, *J* = 7.2 Hz, H_5); ^{13}C NMR δ 117.1 (C_4), 123.2 (C_3), 123.3 (C_5), 124.2 (C_8), 126.5 (C_6), 126.8 (C_2), 126.9 (C_7), 128.3 (C_9), 129.2 ($C_{2'}$ or $C_{7'}$), 129.2, 129.3, 129.4 ($C_{2'}$ or $C_{7'}$), 131.8 ($C_{1'}$), 132.7, 132.8, 136.3 ($C_{1'}$), 137.1 (C_{4a}), 138.7 (C_{4b}), 139.0 (C_{8a}), 141.5 (C_{9a}); MS *m/z* 334, 332 (M^+), 253. Found: C, 72.20; H, 3.68%. Calcd for $C_{20}H_{13}Br$: C, 72.09; H, 3.93%.

1g. ^{1}H NMR δ 6.51–6.57 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.83–6.99 ($H_{2'}$, $H_{7'}$), 7.02 (dd, *J* = 8.4, 2.1 Hz, H_3), 7.25 (dd, *J* = 7.8, 1.2 Hz, H_7), 7.32 (dd, *J* = 7.8, 1.2 Hz, H_6), 7.65 (dd, *J* = 10.2, 2.1 Hz, H_1), 7.67 (dd, *J* = 8.4, 5.1 Hz, H_4), 7.69 (dd, *J* = 7.8, 1.2 Hz, H_5), 7.94 (d, *J* = 7.8 Hz, H_8); ^{13}C NMR δ 111.7 (d, *J* = 24.9 Hz, C_1), 113.4 (d, *J* = 23.2 Hz, C_3), 119.2 (C_5), 120.2 (*J* = 9.2 Hz, C_4), 124.5 (C_8), 126.1 (C_7), 126.9 (C_6), 128.6 (C_9), 129.2 ($C_{2'}$ or $C_{7'}$), 129.4, 129.5 ($C_{2'}$ or $C_{7'}$), 129.6, 132.6, 132.7, 135.6 (C_{8a}), 137.0 ($C_{1'}$), 138.4 (C_{4a}), 138.8 (C_{4b}), 139.9 (d, *J* = 8.9 Hz, C_{9a}), 161.9 (d, *J* = 241 Hz, C_2).

1h. ^{1}H NMR δ 6.53–6.58 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.89–6.99 ($H_{2'}$, $H_{7'}$), 7.26–7.30 (H_7), 7.29 (dd, *J* = 8.1, 2.4 Hz, H_3), 7.33 (dd, *J* = 6.9, 2.1 Hz, H_6), 7.66 (d, *J* = 8.1 Hz, H_4), 7.72 (dd, *J* = 6.9, 2.1 Hz, H_5), 7.93 (d, *J* = 2.4 Hz, H_1), 7.95 (d, *J* = 7.5 Hz, H_8); ^{13}C NMR δ 119.5 (C_5), 120.3 (C_4), 124.5 (C_1), 124.5 (C_8), 126.5 (C_7), 126.7 (C_3), 126.8 (C_6), 128.3 (C_9), 129.2 ($C_{2'}$ or $C_{7'}$), 129.4, 129.6 ($C_{2'}$ or $C_{7'}$), 129.7, 132.0 (C_2), 132.7, 132.8, 137.2 ($C_{1'}$), 137.9 (C_{4a}), 138.3 (C_{8a}), 138.5 (C_{4b}), 139.7 (C_{9a}); MS *m/z* 290, 288 (M^+).

1i. ^{1}H NMR δ 2.46 (Me), 6.46–6.55 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.91–6.99 ($H_{2'}$, $H_{7'}$), 7.14 (dd, *J* = 7.8, 1.2 Hz, H3), 7.23 (dd, *J* = 7.5, 1.2 Hz, H_7), 7.30 (dd, *J* = 7.5, 1.2 Hz, H_6), 7.63 (d, *J* = 7.8 Hz, H_4), 7.70 (dd, *J* = 7.5, 1.2 Hz, H_5), 7.76 (d, *J* = 1.2 Hz, H1), 7.93 (dd, *J* = 7.5, 1.2 Hz, H_8); ^{13}C NMR δ 22.0 (Me), 119.2 (C_8), 119.3 (C_4), 124.6 (C_5), 125.3 (C_1), 126.0 (C_6), 126.7 (C_7), 127.6 (C_3), 128.8, 128.9, 129.6 (C_9), 129.8 ($C_{2'}$ or $C_{7'}$), 129.8 ($C_{2'}$ or $C_{7'}$), 132.5, 132.5, 135.7 ($C_{1'}$), 136.1 (C_2), 137.2 (C_{4a}), 138.4 (C_{4b}), 138.7 (C_{9a}), 139.7 (C_{8a}); MS *m/z* 268 (M^+). Found: C, 93.61; H, 5.98%. Calcd for $C_{21}H_{16}$: C, 93.99; H, 6.01%.

1j. ^{1}H NMR δ 3.89 (Me), 6.46–6.56 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.92–6.95 ($H_{2'}$, $H_{7'}$), 6.88 (dd, *J* = 8.1, 2.1 Hz, H_3), 7.19 (dd, *J* = 7.5, 1.2 Hz, H_7), 7.28 (dd, *J* = 7.5, 1.2 Hz, H_6), 7.51 (d, *J* = 2.1 Hz, H_1), 7.64 (d, *J* = 7.5 Hz, H_5), 7.64 (d, *J* = 8.1 Hz, H_4), 7.90 (d, *J* = 7.5 Hz, H_8); ^{13}C NMR δ 55.5 (Me), 111.6 (C_1), 111.6 (C_3), 118.7 (C_8), 120.1 (C_4), 124.5 (C_5), 125.4 (C_6), 126.8 (C_7), 128.9, 129.1, 129.4 (C_9), 129.4 ($C_{2'}$ or $C_{7'}$), 129.6 ($C_{2'}$ or $C_{7'}$), 132.5, 132.6, 133.0 (C_{4a}), 136.0 ($C_{1'}$), 138.3 (C_{4b}), 139.7 (C_{8a}), 139.9 (C_{9a}), 158.8 (C_2); MS *m/z* 284 (M^+). Found: C, 88.38; H, 5.51%. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67%.

1k. ^{1}H NMR δ 6.60–6.63 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.91–6.94 ($H_{2'}$, $H_{7'}$), 7.44 (dd, *J* = 7.8, 2.1 Hz, H_3, H_6), 7.58 (d, *J* = 7.8 Hz, H_4, H_5), 8.07 (d, *J* = 1.8 Hz, H_1, H_8); ^{13}C NMR δ 120.5 (C_2, C_7), 120.7 (C_4, C_5), 126.9 (C_9), 127.1 (C_1, C_8), 129.2 ($C_{2'}$, $C_{7'}$), 129.4 (C_3, C_6), 130.3 ($C_{3'}$, $C_{6'}$), 133.0 ($C_{4'}$, $C_{5'}$), 137.2 (C_{4a}, C_{4b}), 138.5 ($C_{1'}$), 139.8 (C_{8a}, C_{9a}); MS *m/z* 414, 412, 410 (M^+).

1l. ^{1}H NMR δ 1.39 (Bu), 6.45–6.51 ($H_{3'}$, $H_{6'}$), 6.53–6.56 ($H_{4'}$, $H_{5'}$), 6.90 (d, *J* = 10.8 Hz, $H_{2'}$, $H_{7'}$), 7.34 (dd, *J* = 8.0, 1.5 Hz, H_3, H_6), 7.61 (d, *J* = 8.0 Hz, H_4, H_5), 7.95 (d, *J* = 1.5 Hz, H_1, H_8); ^{13}C NMR δ 31.5 (Me), 34.8, 118.7 (C_4, C_5), 121.6 (C_1, C_8), 124.0 (C_3, C_6), 128.5 ($C_{3'}$, $C_{6'}$), 129.5 ($C_{2'}$, $C_{7'}$), 130.5 (C_9), 132.5 ($C_{4'}$, $C_{5'}$), 134.5 ($C_{1'}$), 137.2 (C_{4a}, C_{4b}), 138.7 (C_{8a}, C_{9a}), 149.0 (C_2, C_7); MS *m/z* 366 (M^+). Found: C, 92.00; H, 8.37%. Calcd for $C_{28}H_{30}$: C, 91.75; H, 8.25%.

1m. ^{1}H NMR δ 1.40 (Bu), 6.52–6.59 ($H_{3'}$, $H_{4'}$, $H_{5'}$, $H_{6'}$), 6.86–6.95 ($H_{2'}$, $H_{7'}$), 7.38 (dd, *J* = 8.0, 1.8 Hz, H_6), 7.41 (dd, *J* = 7.8, 1.8 Hz, H_3), 7.57 (d, *J* = 7.8 Hz, H_4), 7.63 (d, *J* = 8.0 Hz, H_5), 7.98 (d, *J* = 1.8 Hz, H_8), 8.05 (d, *J* = 1.8 Hz, H_1); ^{13}C NMR δ 31.5 (Me), 35.0, 119.1 (C_5), 119.7 (C_2), 120.5 (C_4), 121.6 (C_8), 127.3 (C_1), 128.7 (C_9), 129.1 ($C_{2'}$ or $C_{7'}$), 129.2, 129.4 (C_3), 129.5 ($C_{2'}$ or $C_{7'}$), 129.6, 132.7 ($C_{4'}$, $C_{5'}$), 136.1 (C_6), 136.1 (C_{4b}), 136.6 ($C_{1'}$), 138.3 (C_{8a}), 138.5 (C_{4a}), 140.3 (C_{9a}), 150.1 (C_7); MS *m/z* 390, 388 (M^+). Found: C, 73.96; H, 5.41%. Calcd for $C_{24}H_{21}Br$: C, 74.04; H, 5.44%.

Dehydrogenation of 2b. Methyl derivative **2b** (81 mg, 0.3 mmol) in dry benzene (50 mL) was refluxed with DDQ (238 mg, 1.0 mmol) for 72 h under an argon atmosphere. Upon the usual treatment, oligomeric products (17 mg; mp 274–282 °C; molecular weight by GPC, 840, 5400, 15000, 35000, based on polystyrene standard) were obtained in addition to the recovered **2b** (14 mg, 18%).

9-(Cycloheptylidene)fluorene (3a). Titanium tetrachloride (11 mL, 100 mmol) was added to a suspension of zinc powder (13 g, 200 mmol) in DME (40 mL) at −10 °C under an atmosphere of argon. Upon refluxing the mixture for 2 h, a solution of fluorenone (3.60 g, 20 mmol) and cycloheptanone (11.2 g, 100 mmol) in DME (40 mL) was added at room temperature. After refluxing for 2 h, the mixture was quenched with aqueous K_2CO_3 (10%). The organic matter was purified by column chromatography (hexane, SiO_2) to give 2.11 g (41%) of **3a**: Mp 123–125 °C (ethanol); ^{1}H NMR δ 1.63–1.67 ($H_{4'}$, $H_{5'}$), 1.93–1.96 ($H_{3'}$, $H_{6'}$), 3.01–3.13 ($H_{2'}$, $H_{7'}$), 7.26–7.35 (H_2, H_3, H_6, H_7), 7.75–7.87 (H_1, H_4, H_5, H_8); ^{13}C NMR δ 26.8 ($C_{3'}$, $C_{6'}$), 28.9 ($C_{4'}$, $C_{5'}$), 35.2 ($C_{2'}$, $C_{7'}$), 119.2 (C_4, C_5), 124.9 (C_1, C_8), 126.3 (C_2, C_7, or C_3, C_6), 126.7 (C_2, C_7, or C_3, C_6), 132.1 (C_{8a}, C_{9a}), 138.7 ($C_{1'}$), 139.6 (C_{4a}, C_{4b}), 151.9 (C_9); MS *m/z* 260 (M^+). Found: C, 92.14; H, 7.56%. Calcd for $C_{20}H_{20}$: C, 92.26; H, 7.74%.

9-(2,6-Cycloheptadienylidene)fluorene (4a). A mixture of **3a** (260 mg, 1.0 mmol) and DDQ (550 mg, 2.3 mmol) in benzene (200 mL) was refluxed for 4 h under an argon atmosphere. By a procedure similar to that mentioned above, **4a** (99 mg, 39%) was obtained: Mp 60 °C (ethanol); ^{1}H NMR δ 2.48–2.50 ($H_{4'}$, $H_{5'}$), 6.12–6.15 ($H_{3'}$, $H_{6'}$), 7.06 (d, *J* = 11.4 Hz, $H_{2'}$, $H_{7'}$), 7.26 (td, *J* = 7.4, 1.6 Hz, H_2, H_7), 7.32 (td, *J* = 7.4, 1.6 Hz, H_3, H_6), 7.73 (d, *J* = 7.1 Hz, H_4, H_5), 7.88 (d, *J* = 7.5 Hz, H_1, H_8); ^{13}C NMR δ 26.9 ($C_{4'}$, $C_{5'}$), 119.4 (C_4, C_5), 126.3 (C_1, C_8), 126.5 (C_2, C_7), 127.2 (C_3, C_6), 130.8 ($C_{2'}$, $C_{7'}$), 133.1 ($C_{3'}$, $C_{6'}$), 134.7 (C_9), 137.9 ($C_{1'}$), 138.7 (C_{8a}, C_{9a}), 140.0 (C_{4a}, C_{4b}); MS *m/z* 256 (M^+). Found: C, 93.35; H, 6.40%. Calcd for $C_{20}H_{16}$: C, 93.71; H, 6.29%.

(9-Fluorenyl)tropylium Trifluoroacetate (5a). TFA (0.35 mL) was added to **1a** (35.6 mg) in a NMR tube. After the addition of $CDCl_3$ (0.35 mL), the NMR spectra were measured: ^{13}C NMR δ 58.6 (C_9), 121.4 (C_4, C_5), 125.6 (C_1, C_8), 129.0 (C_2, C_7), 130.0 (C_3, C_6), 141.4 (C_{4a}, C_{4b}), 146.0 (C_{8a}, C_{9a}), 153.5, 153.8, 155.3 ($C_{2'}$, $C_{7'}$), 178.2 ($C_{1'}$).

5d. ^{13}C NMR δ 58.3 (C_9), 121.5 (C_5), 122.4 (C_2), 125.6 (C_4), 125.7 (C_8), 129.0 (C_7), 130.3 (C_6), 133.3 (C_3), 140.4 (C_{4b}), 140.5 (C_{4a}), 145.7 (C_{8a}), 147.4 (C_{9a}), 153.9, 154.1, 155.4 ($C_{2'}$, $C_{7'}$), 176.9 ($C_{1'}$).

5e. ^{13}C NMR δ 58.2 (C_9), 121.7 (C_5), 124.6 (C_3), 124.8 (C_4), 125.8 (C_8), 127.0 (C_1), 129.8 (C_7), 130.3 (C_6), 131.9 (C_2), 140.1 (C_{4b}), 143.6 (C_{4a}), 144.6 (C_{9a}), 146.3 (C_{8a}), 153.9, 154.0, 155.3 ($C_{2'}$, $C_{7'}$), 177.2 ($C_{1'}$).

5f. ^{13}C NMR δ 58.4 (C_9), 118.1 (C_4), 124.7, 125.0, 125.6, 129.6, 129.7, 135.0, 139.8, 140.7, 146.1, 148.0, 154.0, 155.3 ($C_{2'}$, $C_{7'}$), 177.8 ($C_{1'}$).

5g. ^{13}C NMR δ 58.6 (C_9), 113.1 (d, J = 23.9 Hz, C_1), 117.6 (d, J = 23.1 Hz, C_3), 121.2 (C_5), 122.8 (d, J = 8.9 Hz, C_4), 125.8 (C_8), 128.9 (C_7), 130.3 (C_6), 137.8 (d, J = 2.7 Hz, C_{4a}), 140.6 (C_{4b}), 146.0 (C_{8a}), 147.6 (d, J = 8.2 Hz, C_{9a}), 154.0, 154.2, 155.5 ($C_{2'}$, $C_{7'}$), 163.4 (d, J = 248 Hz, C_2), 177.5 ($C_{1'}$).

5h. ^{13}C NMR δ 58.6 (C_9), 121.6 (C_5), 122.4 (C_4), 125.9 (C_8), 126.2 (C_1), 129.5 (C_7), 130.4 (C_6), 130.6 (C_3), 135.0 (C_2), 140.3 (C_{4a}), 140.6 (C_{4b}), 146.0 (C_{8a}), 147.4 (C_{9a}), 154.0, 154.3, 155.6 ($C_{2'}$, $C_{7'}$), 177.3 ($C_{1'}$).

5i. ^{13}C NMR δ 21.1 (Me), 58.4 (C_9), 121.0 (C_5), 121.0 (C_4), 125.6 (C_8), 126.1 (C_1), 128.4 (C_7), 129.8 (C_6), 130.7 (C_3), 138.5 (C_{4a}), 139.5 (C_2), 141.4 (C_{4b}), 145.9 (C_{8a}), 146.3 (C_{9a}), 153.4, 153.7, 155.2 ($C_{2'}$, $C_{7'}$), 178.2 ($C_{1'}$).

5j. ^{13}C NMR δ 56.1 (Me), 58.5 (C_9), 112.2 (C_1), 115.8 (C_3), 120.7 (C_5), 122.4 (C_4), 125.6 (C_8), 128.1 (C_7), 130.0 (C_6), 135.1 (C_{4a}), 140.9 (C_{4b}), 145.6 (C_{8a}), 147.7 (C_{9a}), 153.6, 153.9, 155.3 ($C_{2'}$, $C_{7'}$), 159.4 (C_2), 177.7 ($C_{1'}$).

5k. ^{13}C NMR δ 58.1 (C_9), 122.8 (C_4, C_5), 123.1 (C_2, C_7), 129.2 (C_1, C_8), 133.8 (C_3, C_6), 139.6 (C_{4a}, C_{4b}), 147.2 (C_{8a}, C_{9a}), 154.4, 154.5, 155.6 ($C_{2'}$, $C_{7'}$), 175.8 ($C_{1'}$).

5l. ^{13}C NMR δ 31.0 (Me), 35.1, 59.1 (C_9), 120.8 (C_4, C_5), 122.4 (C_1, C_8), 127.5 (C_3, C_6), 138.8 (C_{4a}, C_{4b}), 146.8 (C_{8a}, C_{9a}), 153.0 (C_2, C_7), 153.5, 153.7, 155.4 ($C_{2'}$, $C_{7'}$), 179.6 ($C_{1'}$).

5m. ^{13}C NMR δ 30.9 (Me), 35.2, 58.5 (C_9), 121.1 (C_5), 121.9 (C_2), 122.4, 122.4, 127.8 (C_6), 129.0 (C_1), 133.3 (C_3), 137.8 (C_{4b}), 140.4 (C_{4a}), 146.0 (C_{9a}), 147.7 (C_{8a}), 154.0, 154.0, 154.1, 155.4 ($C_{2'}$, $C_{7'}$), 177.3 ($C_{1'}$).

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